

CHARACTERIZATION OF COASTAL OPTICAL PROPERTIES THROUGH THE APPLICATION OF FLOW FIELD FLOW FRACTIONATION

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LONG-TERM GOALS

Total optical attenuation in seawater is defined by the following equation (Jerlov, 1968):

$$C_{\text{tot}} = a_p + a_{\text{DOM}} + b_p + c_w$$

where a_p = absorption coefficient for particles, a_{DOM} is the absorption coefficient for the dissolved organic matter, b_p is the scattering by particles, and c_w is the attenuation by water (through absorption, and elastic and inelastic scattering). For coastal waters it is the first three terms of this equation that are responsible for the large range in optical attenuation and variation in color that are often observed. Also, these terms are interactive through a variety of processes involving transformations between the biota, DOM, and particulates. The processes affecting these transformations in coastal environments can be complex and dynamic; they include, but are not limited to recycling, sediment resuspension, precipitation, photochemical alteration, tidal flow and other physical transport and mixing processes.

The emphasis in this study is placed on characterizing the factors affecting the optical properties (i.e. attenuation and fluorescence) of coastal seawater. Particular emphasis is being placed on developing a better understanding of the differences and similarities between colored dissolved organic matter CDOM of marine and terrestrial origin, and the impact these properties have on the chemical and optical characteristics of coastal environments where their effects are most pronounced. The equipment assembled under this grant is being used both in the laboratory and in shipboard experiments to provide detailed characterization of the optical properties of coastal seawater. Such information once acquired can be applied to remote sensing modeling applications and the design of optical sensing detectors for probing the ocean.

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OBJECTIVES

The primary objective is to utilize Flow Field Flow Fractionation (FFFF) in both laboratory studies and in real-time measurements onboard a ship. The field studies will be done in conjunction with other optical measurements performed *in situ*. The FFFF system will provide information on molecular characterization of the CDOM in a water mass and detailed spectral information on absorbance, fluorescence, and optical scattering for colloids or fine particles. In this application the FFFF system should provide near real time information on the optical characteristics of a water mass that could in turn be used for ground truthing in remote sensing applications or as a calibration tool for *in situ* optical sensors. This work is supported by ONR Biological Oceanography and Ocean Optics.

APPROACH

The technique of Flow Field Flow Fractionation (FFFF) has been utilized in preliminary experiments to characterize a series of extracted dissolved organic matter (DOM) samples from riverine, coastal and oceanic regions. Flow FFF utilizes an open channel into which a sample is injected. In this channel the sample is subjected to a transverse flow of carrier fluid. The separation relies on the distribution of the species in the channel cross-section. This distribution is dependent on the diffusivity of the individual species. Following separation, a variety of techniques may be used to detect the size fractionated components. There are many advantages to this technique compared to other techniques of DOM fractionation such as gel permeation chromatography which suffer from adsorptive and charge repulsion effects. This technique allows for the fractionation of the DOM in a matrix similar to seawater. Thus, factors such as ionic strength which affect the conformation of the colloidal DOM can be controlled. This technique offers considerable utility for looking at the optical properties of DOM, as common detectors can be connected in line and highly resolved fractions can be collected for further manipulations (photochemical product studies, EPR, NMR, etc.).

WORK COMPLETED

Most of the components for the FFFF system have been purchased and assembled. The system is now operational and method development for the characterization of CDOM samples is currently underway. The only detection capability available to this point is UV-visible absorbance. Fluorescence and fluorescence lifetime detection components should be added to the system within the next two months. The addition of these components will complete the assembly phase of the FFFF system. A coastal cruise aboard the R. V. Calanus was successfully conducted during the last year to provide samples for the FFFF system.

RESULTS

Early results from the application of the technique of FFFF for the characterization of colored dissolved organic matter (CDOM) samples indicate that very different results are obtained when compared to other more traditional separation techniques (e.g. gel permeation chromatography). Work is underway to determine optimal separation conditions and to establish procedures for producing detailed optical characterization of the fractionated CDOM from various environments. Both optical absorption and fluorescence properties will be measured. This should prove to be a novel and very useful technique for understanding the complex optical properties of aquatic CDOM.

IMPACT

Flow FFF and the associated measurements have the potential to greatly improve our understanding of the chemistry and physics of light in the ocean. The development of this as a new analytical technique for marine studies can provide a technique that is useful for in many other applications. Flow FFF coupled with recent enhanced computer processing capabilities can provide for high frequency sampling with near real time data acquisition.

TRANSITIONS

The results from this work and other related studies show that our understanding of CDOM and its effects on the optical properties of the ocean and particularly coastal ocean are marginal. The lack of such information dramatically limits the application of strategic approaches to remote and in situ observational methods such as satellites or submerged detection systems. Understanding the chemical and physical characteristics of the CDOM is essential for the development of accurate optical methods and modeling tools. This is particularly true for coastal environments.

RELATED PROJECTS

The cruises during the last year have involved ONR funded investigators from optical physics, marine biology and marine chemistry. A thorough understanding of the nature of CDOM in the oceans requires a multi-disciplinary approach. Future endeavors should also include the area of remote sensing.

REFERENCES

Jerlov, N. G., Optical Oceanography Elsevier Oceanography Series Vol. 5, Elsevier. Amsterdam 194 pp. 1968.